Clathrate hydrate equilibria of methane and ethane

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Introduction

Equilibrium conditions of clathrate hydrate containing hydrocarbon gases are important to natural gas hydrate stability in marine sediment. Natural gas hydrate often contains methane with higher hydrocarbons such as ethane and propane. The ethane concentration up to 10 % was observed in natural gas hydrate containing thermogenic gases, for example, sampled in the Gulf of Mexico. On the other hand, it is known that clathrate hydrate equilibria of methane and ethane mixture are different from that of pure methane. In this work, clathrate hydrate equilibria of methane and ethane mixtures in pure water and NaCl solutions whose salinity is similar to seawater were experimentally determined. The experimental data were used to develop the statistical thermodynamic model of clathrate hydrate proposed by van del Waals and Platteeuw.

Results and Discussion

In this work, clathrate hydrate equilibria of methane and ethane mixtures with ethane compositions of 1%, 2%, 5%, 10% and 20% in pure water and 3wt% NaCl solution were experimentally determined. The results indicate that the addition of ethane to methane trapped in gas hydrate lattice shifts the hydrate equilibria to higher temperature and lower pressure and that the hydrate equilibrium decreases non-proportionally as ethane concentration in the mixture increases, which implies a hydrate structural change of Structure I to Structure II in ethane compositional range between 1% to 2%. The results also indicate that the equilibrium temperature differences of the hydrate in pure water and 3wt% NaCl solution are approximately 1 K over the compositional range investigated in this work.

Thermodynamic Modeling

The statistical thermodynamic model of clathrate hydrate proposed by van del Waals and Platteeuw was used to investigate the experimental results in this work. The intermolecular parameters between water and gas in the hydrate lattice, Kihara parameters, were optimized to fit the hydrate equilibrium conditions and implied structural change.

References

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Lithium isotope composition of arc volcanics from the Mt. Shasta region, N California

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Lithium isotopes can provide powerful constraints on the origin of the components in arc magmas. This is because of distinct isotopic signatures for altered oceanic crust and its eclogite residues [1]. Here we report lithium isotope ratios for high-Al olivine tholeiites (HAOT), basaltic andesites (BA), andesites and dacites from Mt. Shasta, Northern California. Lithium isotopes have been measured on Nu1700, a large geometry high-resolution mass spectrometer. Long-term reproducibility of international reference rock standards such as JB-2, AGV-2, or BHVO-2 is better than 0.5 ‰ (2 SE) [2].

The subset of Mt. Shasta region lavas does not show much evidence of fractional crystallization, crustal contamination or magma mixing [3]. Therefore, the observed range of δ^7Li values from 2.5 to 6.5 ‰ relative to L-SVEC most likely reflects distinct mantle components. The lowest δ^7Li values from 2.5 to 3.5 ‰ characterise near-anhydrous HAOT lavas erupted through the arc and back arc region towards the east of Mt. Shasta. HAOTs are thought to be generated by decompression melting of spinel lherzolite. However, lithium isotopes are inconsistent with models that assume melting of an old metasomatized peridotitic mantle source [4] because fluids in a subduction zone are thought to be ^{7}Li-enriched. δ^7Li values as low as –10‰ are reported for eclogites. Admixing ≤ 2 % of such eclogite to the mantle sources could explain low δ^7Li values of HAOTs. This is consistent with for example, the relatively radiogenic lead and the high concentrations of heavy rare earth elements (20 times chondritic) in HAOTs. δ^7Li values of BAs vary between 4.0 and 6.5 ‰. The lithium isotope composition of BAs is consistent with mixing Li into a former depleted mantle source by fluids derived either from low-T altered oceanic crust or sediments. Both HAOT and BA lavas form a linear array in δ^7Li-Y/Li space consistent with decoupling of Y and Li by fluid processes. Andesites and dacites show the same range of Li isotope ratios as BAs. Therefore, Li isotopes are consistent with generation of andesites and dacites from the same source as BAs.

References

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